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Modulus of Elasticity of Alloys

THE stiffness of beams and other structural members is dependent on the modulus of elasticity of the materials employed, and this property has become increasingly important to designers with the continual improvement in the strength of alloys which has provided engineers with the possibility of greater lightness of construction.

Alloy steels are capable of supporting higher working stresses than mild steel, but within the safe working stresses their use confers no increase in rigidity. The elastic moduli of all steels are approximately equal, and if a certain elastic deflection must not be exceeded in a structure, alloy steels offer no saving in weight over mild steel. The sections employed must be the same for each material. The modulus of a light alloy is to that of steel in the approximate ratio of their densities. Hence, aluminium alloy beams must be deeper than corresponding steel beams to preserve the same stiffness. This sometimes means that the high strength of certain light alloys cannot be completely utilised because of limitations in the permissible deflection under load.

A comprehensive experimental study of the modulus of elasticity of metals and alloys has been made by L. Guillet, jun.* The modulus in tension was determined by the Rolland-Sorin method, which depends on the sympathetic vibration of two equal pendulums hanging from the ends of a short platform secured to the bottom of the test specimen which is clamped in a vertical position at the upper end. While one pendulum (P1) is stationary, the other (P2) is set in motion. The oscillations of P2 diminish, while those of P1 increase to a maximum at the moment when P2 is stationary, and then die away again as those of P2 increase. If t is the time between two successive stationary conditions of the pendulum P1 and E is the modulus of elasticity of the test specimen, then $E = k\,t$. The value of the constant k is determined by calibrating the instrument by tests on metals of known elastic modulus; for example, aluminium, copper, platinum, and mild steel. The calibration curve of modulus against time interval between stationary conditions is a straight line, and the value of E, for an observed value of t, can be readily ascertained. The method has the advantage that small specimens can be used. The bars employed were 60 mm. long and 5·64 mm. in diameter, or 25 square millimetres in cross sectional area. Cast bars were radiographed before they were tested to ensure that sound material was being used.

The values obtained for the moduli of the metals are given in Table I, together with the atomic volumes V and melting points T. The modulus E, plotted against $1/V^2$, gives points scattered about an approximate straight line. If E is plotted against T/V^2 the scatter is reduced, but the relation is far from accurate, and merely indicates that a high modulus is to be found in elements of high melting point, whose atomic value is low. Although the modulus of beryllium was known by the atomic volume relation to be high and in the vicinity of 30,000 kilos. per square millimetre, the value given in the table is claimed to be the first experimental determination of the value for metallic beryllium, the density of which was found to be 1·85. The sample contained about 97·8 per cent. of beryllium.

TABLE I.—*Modulus of Elasticity of the Metals*

	Atomic volume.	Melting point, deg. Cent.	Modulus of elasticity.	
			Kilos. per sq. mm.	Lb. per sq. in.
Tungsten ...	9·6	3,660	42,000	$59·7 \times 10^6$
Beryllium ...	4·9	1,278	36,000	51·2
Iron...	7·1	1,530	21,000	29·8
Nickel	6·6	1,451	22,000	31·3
Platinum ...	9·1	1,771	16,300	23·2
Copper	7·1	1,083	12,600	17·9
Silicon	12·2	1,425	9,500	13·5
Gold	10·2	1,063	8,500	12·1
Zinc...	9·2	420	8,000	11·4
Silver	10·2	961	7,000	10·0
Aluminium ...	9·9	658	7,300	10·4
Magnesium ...	13·9	651	4,500	6·4
Tin	16·3	232	4,000	5·7
Calcium	26	809	2,000	2·8
Lead	19	327	1,800	2·6

The alloys investigated included the solid solutions of copper with zinc, aluminium, and tin. In each case the alloy addition regularly diminishes the modulus of copper. The reduction in modulus was a linear function of the tin or zinc content, and also of aluminium content when this was expressed as per cent. by volume. Addition of iridium or of rhodium to platinum increased the modulus, again in an approximately linear manner. The value 16,300 kilos. per square millimetre for platinum was raised to 20,300 kilos. and 21,850 kilos. per square millimetre by the addition of 15 per cent. of iridium and of rhodium respectively.

Intermetallic compounds fell into two groups:—(1) Those with metallic characteristics in which the modulus agreed with that calculated by the law of mixtures, *e.g.*, CuZn, $CuAl_2$, Cu-Au, &c.; and (2) the

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homopolar compounds, such as Cu_5Zn_8, $Cu_{31}Sn_8$ in which the modulus was considerably higher than the value calculated in this way, and in some instances higher than that of either constituent. For example, Cu_9Al_4 (copper 84·25 per cent.) had a modulus of 16,850 kilos. per square millimetre. All such compounds, however, are extremely brittle.

Alloys consisting of two phases, *e.g.*, a solid solution and a compound, also showed a linear relation between the two phases. Beryllium causes a marked rise in the modulus of copper, thus :—

Beryllium, per cent.	Modulus of elasticity, kilos. per sq. mm.	lb. per sq. in.
0	12,600	$17·9\times10^6$
4·6	14,500	20·6
10·6	17,000	24·2
12·4 (CuBe)	18,000	25·6
16·6	20,400	29·0
22·1 ($CuBe_2$)	22,800	32·4

Other examples are given in Table III. The effect of aluminium and magnesium on one another is very slight. Copper raises the modulus of aluminium continuously up to 45·7 per cent. ($CuAl_2$), when the value is 9640 kilos. per square millimetre, and over the whole range of composition, aluminium to copper, there were abrupt changes in direction of the modulus curve when the two phases changed, with a maximum at Cu_9Al_4, as indicated above.

The influence of heat treatment on the modulus was studied. In the commercially important alloys the modulus was very little affected by heat treatment, but in alloys containing intermetallic compounds changes could be brought about which affected the modulus considerably. For example, the suppression of the separation of $Cu_{31}Sn_8$ by quenching copper-tin alloys with 22 to 32 per cent. of tin caused a considerable reduction in the modulus which reverted to its original value on reheating. On the other hand, the variation in modulus obtained by quenching and tempering a 2·5 per cent. beryllium-copper alloy was only about 6 per cent., the values obtained being as follows :—

	Brinell hardness number.	Modulus of elasticity, kilos. per square mm.
Water-quenched from 800 deg. Cent.	120	12,600
Reheated 3 hours at 320 deg. Cent. and slowly cooled	360	13,570

The increase in modulus produced by temper hardening is thus less than has sometimes been suggested.

In a 0·83 beryllium-aluminium alloy the change in modulus on ageing was even smaller :—

	Brinell hardness number.	Modulus of elasticity, kilos. per square mm.
Water-quenched from 630 deg. Cent.	25	7,500
Aged	40	7,600

Ageing of this alloy takes place very rapidly, being complete in about one hour at room temperature.

The investigation, in addition to providing some useful data on the influence of composition on the modulus of elasticity of commercial alloys, has confirmed the widely held conclusion that small variations of composition and the presence of impurities have a negligible effect on the modulus of elasticity of a metal or alloy. Except in certain series of solid solutions, exemplified by the platinum-rhodium alloys, it would appear to be impossible to effect a notable improvement in the modulus of elasticity of a metal by alloy additions, since even if the added element itself has a high modulus, its presence in

TABLE II.—*Modulus of Elasticity of Copper Alloys*

Copper-Aluminium.			Copper-Zinc.			Copper-Tin.		
Al, per cent.	Modulus of elasticity.		Zn, per cent.	Modulus of elasticity.		Sn, per cent.	Modulus of elasticity.	
	Kilos. per square mm.	Lb. per square in.		Kilos. per square mm.	Lb. per square in.		Kilos. per square mm.	Lb. per square in.
0	12,600	$17·9\times10^6$	0	12,600	$17·9\times10^6$	0	12,600	$17·9\times10^6$
2·05	12,260	17·4	9·79	12,060	17·1	1·92	12,300	17·5
4·72	11,920	17·0	19·36	11,600	16·5	3·81	12,000	17·1
5·80	11,750	16·7	25·25	11,380	16·2	6·05	11,620	16·5
7·90	11,650	16·5	34·76	10,970	15·6	8·02	11,350	16·1
9·87	11,350	16·1	37·33	10,830	15·4	9·90	10,900	15·5

TABLE III.—*Modulus of Elasticity of Light Alloys*

Aluminium-Copper.			Aluminium-Magnesium.			Magnesium-Aluminium.		
Cu, per cent.	Modulus of elasticity.		Mg, per cent.	Modulus of elasticity.		Al, per cent.	Modulus of elasticity.	
	Kilos. per square mm.	Lb. per square in.		Kilos. per square mm.	Lb. per square in.		Kilos. per square mm.	Lb. per square in.
0	7,300	$10·38\times10^6$	0	7,300	$10·38\times10^6$	0	4,500	$6·40\times10^6$
2·18	7,300	10·38	2·29	7,240	10·30	2·10	4,660	6·63
2·58	7,480	10·64	4·18	7,280	10·35	4·58	4,720	6·71
6·47	7,500	10·67	5·80	7,300	10·38	6·88	4,750	6·75
7·90	7,620	10·84	8·00	7,200	10·24	8·00	4,830	6·87
10·20	7,680	10·92	10·07	7,150	10·17	9·28	4,790	6·79
12·85	8,030	11·42	11·93	7,120	10·13	12·15	4,860	6·91

quantities sufficient to produce a substantial increase in the modulus is usually accompanied by phase changes which render the alloy unsuitable for commercial purposes.

The Adhesion of White Metal to Bronze

An essential requirement of white metal bearings is that there should be a very good bond between the alloy or lining, and its container or shell. Lack of adhesion leads to failure by the shell to conduct away heat generated by friction in the lining, with the result that the operating temperature becomes excessively high, while at the same time stresses are imposed which the anti-friction alloy will not withstand. D. J. Macnaughtan[1] found that stresses produced by flexure of the lining when the adhesion is imperfect led to cracking and failure of the white metal, which otherwise would have functioned satisfactorily. Spreading or extrusion of the metal from the bearing is also more pronounced when adhesion is poor, or, in other words, the effective compression strength of the white metal is reduced by lack of adhesion. The serious effects of imperfect adhesion are referred to by H. N. Bassett,[2] and there is little doubt that faulty adhesion of white metal to bronze is one of the chief causes of cracking and failure of white metal in engine and wagon bearings.

For this reason an investigation was undertaken by Mr. K. Ray,[3] of the Metallurgical Inspectorate, Indian Stores Department, with the object of studying the technique of bonding white metals to bronze, with special reference to the Indian Railway Standard Alloys. The investigation was carried out in three stages. In the first the I.R.S. anti-friction alloys, Classes I, III, and IV, were bonded to the I.R.S. bronze, Class II, with pure tin as the medium of bonding, and with some slight variations in fluxes. In stage two the same alloys (and one additional anti-friction alloy) were used with a tin-lead solder as the medium for bonding, but more attention was paid to certain details, such as solder, flux, temperature control, &c. In the third stage a wider variety of alloys was employed, one standard technique of bonding being followed throughout. In the first stage tensile tests only were made at atmospheric temperatures and at 85 deg. Cent. In the second and third stages tests were also made in compression and shear. To these tests was added examination of the microstructure. The composition of the materials used is given in Table I :—

Table I.—*Composition Per Cent. of the Materials Used*

	Tin.	Antimony.	Copper.	Lead.
I.R.S. anti-friction alloy :				
Class I... ...	58–60	11–13	5·5–6·5	19·5–24·5
Class III ...	5·5–6·5	12–14	1–1·5	77–80·5
Class IV ...	79·5–83·5	9–11	5–6	2–3
E.I.R. "G" metal	30	—	5	Zinc 65
B.B. and C.I.R. loco. metal ...	30	15·5	1·5	53
B.B. and C.I.R. electric stock bearing metal...	23	16·5	1	59·5
I.R.S. bronze :				
Class I... ...	10–12	—	86·4–88·6	Phosphorus 0·4–0·6
Class II ...	9–11	—	88–90	—
Class III ...	8–10	—	73–77	14–16

Test bars, 11in. long and 1in. diameter, of the various classes of I.R.S. bronzes were cast and machined to size. Each test bar was cut exactly in the middle and the ends were smooth machined, thus forming two test pieces to be bonded with white metal. The two test pieces were cleaned properly and one end of each was tinned. The test pieces and the split steel mould (Fig. 1) were separately heated to a suitable temperature in an electric muffle. The tinned ends were inserted in the split mould so that they faced each other, separated by a distance of ¼in., and the white metal was poured in from above. The bonded test pieces were withdrawn from the mould and the excess of white metal was machined off. The tensile tests on the bond were carried out at atmospheric temperature and in an electrically heated jacket at 85 deg. Cent. Compression tests, normal to the plane of the bond, were made on specimens, 0·5in. long, machined across a broken tensile test piece to include the white metal and bronze on each side of the unbroken bond. By shaping the ends of the bronze test pieces in an oblique manner and then bonding in the usual way, compression tests were obtained in which the bond was inclined at a predetermined angle to the normal, and oblique compression tests or tests of the bond in shear were thus made, the magnitude of the stress tangential to the bond being calculated.

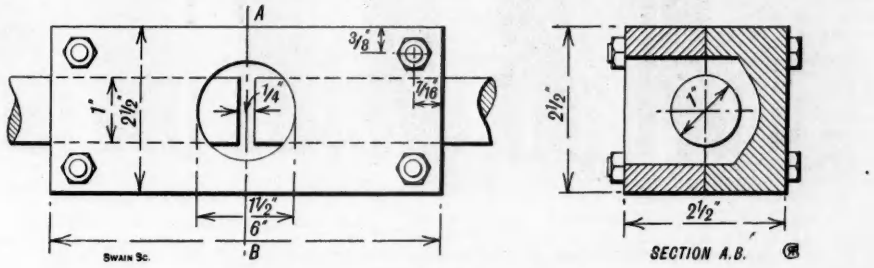

Fig. 1—*Mould for White Metal Bonding*

Cleaning and Tinning

For tinning, a 50 : 50 tin-lead solder was found to be as good as pure tin. A 50 : 50 tin-lead solder with 3 per cent. of antimony was tried, but without success. The procedure for tinning which was found

most satisfactory and adopted in the final comparative trials was laid down by the author in the following terms :—

A newly machined surface to be tinned should be thoroughly cleaned with warm caustic soda (5 to 10 per cent.), soap and water. A tarnished surface should be pickled, in addition, in warm 10 per cent. sulphuric acid, followed immediately by treatment with the caustic soda solution. After cleaning, the article to be tinned should be heated to the temperature of the tin bath in a short time without allowing oxide films to form again. A moderately greasy flux (*e.g.*, fused zinc chloride and ammonium chloride in the proportion 7 : 3 mixed with twice as much petroleum jelly) should be applied to the clean surface of the article with a soft brush before it is dipped in the tin bath (50 : 50 tin-lead solder at 240 deg. to 245 deg. Cent.). In 2 min. the article should be taken out, refluxed with the same flux and the first tin coating should be vigorously rubbed with a wire brush, after which a second dipping should be given.

The tin coating should be rubbed a third time (but this time with a soft brush), using a 25 per cent. solution of a mixture of zinc chloride and ammonium chloride in the ratio of 7 : 3 as a flux. The article should be dipped again. When it is finally withdrawn from the tin bath, the tin coating should be lightly brushed with the 25 per cent. solution of the chlorides, wiped with a piece of clean rag and the white metal poured in 2–3 minutes. This time interval should not be varied considerably. The jelly chloride flux and the 25 per cent. solution can be substituted by a simpler flux made up with 25 parts of zinc chloride, 4 parts of hydrochloric acid, and 96 parts of water, which can be used right through the operation. Contamination by grease must be avoided in the last tin coating.

The following pouring and mould temperatures gave the best results, *i.e.*, those associated with the maximum tensile strength :—

Type of alloy.	Temperature (deg. Cent.). Of metal.	Of mould.
Class III, about 80 per cent. lead...	380	165
Class IV, about 80 per cent. tin ...	415	175
Class I, about 60 per cent. tin ...	410	175

TESTS OF ADHESION

The strongest bonds were obtained with the I.R.S. alloy, Class I (tin 60, lead 20 per cent.) and I.R.S., bronze, Class III (lead bronze), the average tensile strength of adhesion being 6·28 tons per square inch, and the maximum value obtained 6·56 tons per square inch. The highest value previously recorded by any other investigator for the tensile strength of adhesion of white metal to bronze is 5·80 tons per square inch.[4]

Equally strong bonds were obtained with I.R.S. alloy, Class IV (tin 80 per cent.), and I.R.S. bronze, Class II, but the average value was slightly lower than with Class I alloy and Class III bronze. The maximum value, 6·56 tons per square inch, obtained both with Class I and Class IV alloys, was equal to the highest recorded value for the tensile strength of the white metal, so that in the ideal case the strength of the bond is equal to that of the lining, a condition confirmed by the fact that fracture occurred half through the bond and half through the metal, giving the above tensile value.

Both the I.R.S. bronzes, Classes II and III, were suitable for bonding, though a slight preference should be given to Class III (lead bronze) in bonding Class III and Class I alloys. The I.R.S. bronze, Class I (phosphor bronze), was unsuitable, and gave distinctly weaker bonds with all three of the I.R.S. white metals. The I.R.S. alloy, Class III (lead 80 per cent.), gave weaker bonds than the Class I or Class IV alloy, the tensile strength being only about 2·0 tons per square inch. The 30 per cent. tin alloy was rather better, but not so good as the alloys of Classes I

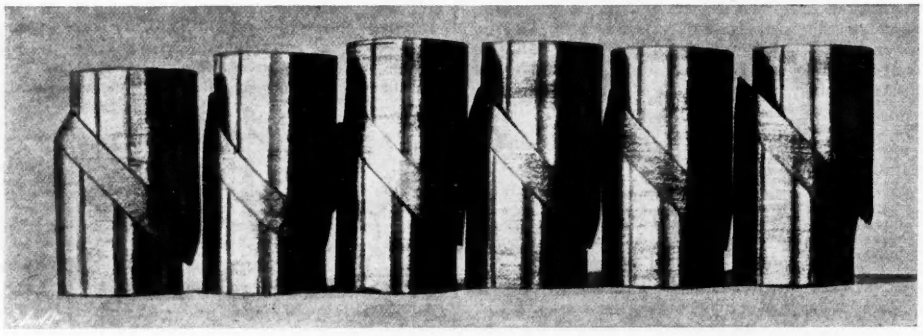

FIG. 2—*Compression Test Pieces*

The bond was unbroken in all test pieces except in the third from the left. × 0·9 (approx.)

TABLE II.—*Particulars of Compression Test Pieces Shown in Fig. 2*

Specimen.	Stress at which bulging commenced.	Stress at which sliding commenced.	
	Compression, tons per square inch.	Compression, tons per square inch.	Equivalent stress tangential to the bonding plane.
1	8·6	10·0	5·0
2	8·6	9·4	4·7
3	7·3	7·3	3·65
4	8·0	8·0	4·0
5	7·2	7·2	3·6
6	6·6	6·6	3·3

No. 3 bond broke before bulging commenced, fracture showed entrapped charcoal powder.
Nos. 4 to 6, bulging and sliding began simultaneously.

and IV. It gave an average tensile strength of 3·0 tons per square inch, while that of the 23 per cent. tin alloy was 1·54 tons per square inch. The E.I.R. "G" metal (65 per cent. zinc) gave very weak bonds with an average tensile strength of only about 1·16 tons per square inch.

Compression tests gave confirmatory indications, the Class IV alloy showing the best results with Class II bronze. The appearance of the "oblique" compression test pieces is shown in Fig. 2. These are duplicate test pieces of (left to right) Class IV (high tin), Class I (medium tin), and Class III (high lead) alloys, bonded to I.R.S. bronze, Class II. The white metal deformed considerably under increasing load, but the bonding remained unbroken except in specimen No. 3.

The stresses to which these specimens had been subjected are given in Table II.

Structure of the Bond

The properties of the bond were further examined by observations of the microstructure. White metal cannot form a continuous bond with a bronze surface if it is cast on to it direct, and in order to obtain a continuous tin-copper layer on the bronze surface, it is essential that the tinning operation should be repeated two or three times with suitable fluxing and brushing. Layers of the ε and η phases of the copper-tin alloys are thus built up and the third layer of the bond obtained in the process of tinning gives a suitable alloy layer to which the white metal can bond when cast on to it. If the white metal has a tin-rich matrix, it readily forms a strongly adhering alloy with the tin coating of the bronze. This applies to the alloys of Class IV and Class I (80 and 60 per cent. of tin respectively), which have tin-rich solid solutions as matrix. The alloys of Class III (80 per cent. lead) have a lead-antimony or lead-tin-antimony eutectic as matrix, and this forms an imperfect alloy with the tin-rich layer on the bronze, and so gives a weak bond.

A second factor which influences the strength of the bond is the difference in the range of solidification temperatures of the various types of white metal. A short freezing range is best. Thus in the Class IV alloy (80 per cent. tin), apart from a small amount of η or CuSn which separates at a higher temperature, solidification occurs over the range 248 deg. to 232 deg. Cent. On the other hand, E.I.R. "G" metal, with a high proportion of zinc, has a much longer freezing range and undergoes a considerable amount of contraction during solidification. Zinc, moreover, readily forms oxide films which seriously interfere with proper bonding. For a similar reason it is found to be very difficult to bond white metals successfully to brass. It was observed in the course of the work that the strength of the bond is largely affected by the percentage of tin in the white metal; the higher the tin content, the stronger the bond. Below a certain percentage of tin, *e.g.*, 30 per cent., the alloys do not give stronger bonds than the I.R.S. alloy, Class III, with 6 per cent. of tin, since they all have a fair amount of free primary lead deposited along the bond layer, thus diminishing the opportunity for the tin-rich matrix to form a strong bond.

This work constitutes one of the most comprehensive series of experiments so far carried out on the adhesion of white metals to bronze, and although it was primarily designed to meet conditions arising in the Indian railways, it has a very considerable importance, both practical and theoretical, to all engineers and metallurgists interested in bearing metals.

References

[1] *Journal of the Institute of Metals*, 1934, 55, 39.
[2] "Bearing Metals and Alloys," Ed. Arnold and Co., London, 1937, 182–186.
[3] "Adhesion Strength of White Metal to Bronze," by K. Ray, M.Sc., A.I.C., Government of India Press, New Delhi, 1939, price 2s. 3d.
[4] E. G. Soash, *Metals and Alloys*, December, 1934, 5, 268.

Grain Size and Critical Cooling Rate of Iron-Carbon Alloys

The critical cooling rate and hardenability of a steel at the time of quenching depend primarily upon three factors, viz., chemical composition, chemical homogeneity, and grain size. The preparation of a supply of very pure carbon steels at the Bureau of Standards some years ago enabled Mr. T. G. Digges to make a study of the influence of carbon content alone on the critical rates of cooling. These rates were found to be four times as great as in commercial products of corresponding carbon content. Even in these very pure steels (in which elements other than iron and carbon were only 0·03 per cent.), the results were influenced by variables other than the carbon content of the materials.[1] One of these was homogeneity of the austenite grains and the rate of transformation of these high-purity steels was subsequently studied in relation to this factor.[2] In the course of this work it was found that in a homogeneous grain the austenite in the vicinity of the boundary is least stable and on quenching transforms at a higher temperature than the more stable austenite in the interior of the grains. It follows that the larger the grain size the more stable the austenite and the deeper the hardening of the alloy, a conclusion in agreement with the recognised relationship between austenitic grain size and hardenability.

"The Influence of Austenitic Grain Size on the Critical Cooling Rate of High-purity Iron Alloys" is the subject of the latest paper by T. G. Digges.[3] The small specimens of the alloys for test (0·1in. square and 0·04in. thick) were heated *in vacuo* or in an atmosphere of dry nitrogen and quenched in a stream of hydrogen. The preliminary heating *in vacuo*, which was the author's practice in previous work, was abandoned in most cases in favour of heating in nitrogen, as it was found that when the hydrogen was admitted into a vacuum the variation in the rate of flow of the quenching gas around the specimen during a short interval after the start of the quench induced an apparent arrest point at about 350 deg. Fah. below the quenching temperature. This arrest (which could be observed in a platinum specimen heated *in vacuo* and quenched in hydrogen) had no appreciable effect on the rate of transformation of the austenite provided that the quenching temperature was well above the critical range on heating. It was found important, however, that specimens quenched from just above the critical range should be heated in an atmosphere of dry nitrogen and not *in vacuo*.

With the equipment described it was possible to heat the specimen at various rates to different temperatures and to quench directly from these temperatures without moving the specimens. The structure produced in the quenched specimens indicated that they were cooled uniformly over the entire surface. For the determination of the critical cooling rates,

a photographic record of the cooling curve was obtained during the quench by means of a string galvanometer in the manner previously described by H. J. French and O. Z. Klopsch.[4] A continuous time-temperature cooling curve could be plotted from the data recorded on the film.

AUSTENITIC GRAIN SIZE

It was essential first to standardise the treatment necessary to give the required grain size. The grain size established at temperatures ranging from 1425 deg. to 1600 deg. Fah. (774 deg. to 871 deg. Cent.) increased markedly with decrease in the rate of heating through the critical range, whereas the grain size at 1800 deg. Fah. (982 deg. Cent.) was not so noticeably dependent on the rate of heating. The grain sizes at temperatures ranging from 1425 deg. to 2100 deg. Fah. (774 deg. to 1148 deg. Cent.) were determined for the alloys. For any temperature within the range from 1600 deg. to 2100 deg. Fah., and with the heating rate employed, all the alloys were found to have approximately the same average grain size, provided that the carbon was completely dissolved. Thus, carbon in solution was not effective in inhibiting grain growth of the austenite in the high purity iron-carbon alloys. For example, at 1700 deg. Fah. (927 deg. Cent.) each of the alloys ranging in carbon from 0·23 to 1·21 per cent. had an average austenitic grain size of 6 to 9 grains per square inch at 100 diameters magnification. The dominant factors in controlling the austenitic grain size of these alloys were the rate of heating through the transformation range and the actual temperature to which they were heated.

CRITICAL COOLING RATE

The hardenability of a steel depends on the stability of the quenched austenite in the approximate temperature range 1110 deg. to 930 deg. Fah. (600 deg. to 500 deg. Cent.). This is the upper range (Ar′) in which decomposition of the austenite results in a relatively soft product. If, by a continuous quench to room temperature, the austenite is cooled through this range without decomposing, it transforms only in the temperature range below about 300 deg. Fah. (149 deg. Cent.), and the product is martensite. If the austenite is cooled at a slower rate through the upper temperature range, part transforms to troostite (fine pearlite) and the remainder cools unchanged to the temperature favourable to its decomposition to martensite. At some cooling rate, called the critical cooling rate, the austenite only just begins to decompose in the range 1110 deg. to 930 deg. Fah. This rate is an index to the stability of the austenite in this temperature range. The slower the critical cooling rate of a steel the more stable is its austenite and the deeper is the hardening.

In the work of Digges the critical cooling rate was taken as the average rate of cooling between 1110 deg. and 930 deg. Fah., which produced, in the quenched specimen, a structure of martensite with nodular troostite in amounts estimated to be between 1 and 3 per cent.

TEMPERATURES OF TRANSFORMATION

In general, the start of Ar′ occurred within the range 1110 deg. to 930 deg. Fah. for all the alloys, provided that they were cooled at the most rapid rate possible for the austenite to transform completely to troostite. For example, the 0·80 per cent. carbon alloy, cooled at 400 deg. Fah. per second, began to transform at 1090 deg. Fah. (588 deg. Cent.); the evolution of heat accompanying the transformation caused a rise in temperature of 45 deg. Fah. in 0·2 second, and a further 0·2 second elapsed before the temperature had again fallen to 1090 deg. Fah., and the normal rate of cooling was resumed. A small amount of austenite was retained through the Ar′ range, as the microstructure showed a trace of martensite in a matrix of troostite. With progressive increase of cooling rate, the amount of austenite which transforms in the Ar′ range is decreased, the heat effect of the Ar′ transformation being diminished in intensity and the temperature of the start of Ar′ slightly lowered. With a cooling rate which produces 5 to 10 per cent. of troostite, the start of Ar′ is at 1040 deg. Fah. With rates in excess of the critical rate, all the austenite is cooled unchanged through the Ar′ range, and transforms to martensite* at Ar″.

The temperature of the start of Ar″ was progressively decreased, with increase of carbon content,

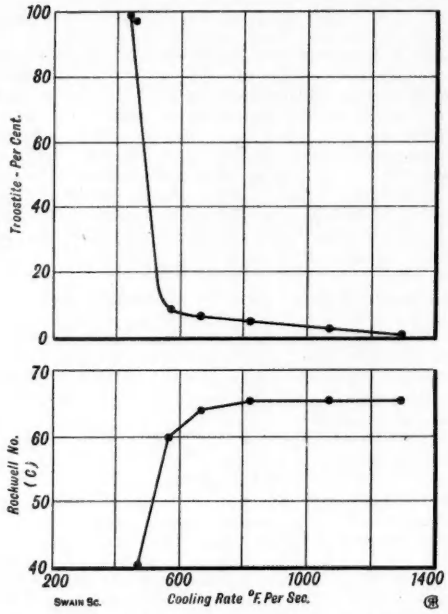

FIG. 1—*Effect of Cooling Rate on the Structure and Hardness of the Iron-Carbon Alloy containing 0·80 per cent. of Carbon quenched from 1425 deg. Fah.*

from about 900 deg. Fah. (482 deg. Cent.) for 0·23 per cent. carbon to 500 deg. Fah. (260 deg. Cent.) for 0·8 per cent. carbon. Increase in quenching temperature from 1425 deg. to 1800 deg. Fah (with corresponding increase in grain size) had no appreciable effect on Ar″ and neither did variation of cooling rate from 550 deg. to 2600 deg. Fah. per second. In the 0·8 per cent. carbon alloy quenched from 1425 deg. Fah. with this variation in rate of cooling, the temperature of the start of Ar″ fell from 500 deg. to 460 deg. Fah.

HARDNESS OF THE QUENCHED ALLOYS

The influence of rate of cooling on structure and hardness of the 0·8 per cent. carbon alloy, quenched

* The martensite transformation is referred to by Digges as Ar″, though it is preferably designated Ar‴, A″ being used for the intermediate transformation which occurs in alloy steels, but not in carbon steels. The term Ar″ is here retained in the sense used by Digges.

from a temperature of 1425 deg. Fah., is indicated in Fig. 1. The critical cooling rate (troostite under 3 per cent.) is about 1250 deg. Fah. per second, but the hardness is almost constant above 700 deg. Fah. per second. An appreciable amount of troostite may be produced in the quenched specimen before its presence is indicated by hardness tests. The hardness value alone cannot be used as an indication of the structural effects produced by different rates of cooling.

The maximum surface hardness of specimens cooled at the critical cooling rate was determined. Some typical results were as follows :—

Carbon, per cent.	Rockwell "C" hardness.	Equivalent Vickers hardness.
0·23	41	404
0·40	53	598
0·62	64	885
0·80	67	1000
1·21	65	930

Up to 0·6 per cent. of carbon these hardness values were considerably lower than those found by J. L. Burns, T. L. Moore, and R. S. Archer[5] for steels of similar carbon content (Rockwell "C," 49 to 66), whereas in the higher carbon range the alloys had approximately the same hardness values as the steels. The maximum hardness attainable on the surface was not influenced by wide variations in grain size and temperature of quenching.

EMPIRICAL RELATIONS

There is a decrease in critical cooling rate (resulting in 1 to 3 per cent. of troostite), with increase in the quenching temperature. This effect was found to be due solely to austenitic grain size. The results for two different grain sizes are shown in Fig. 2.

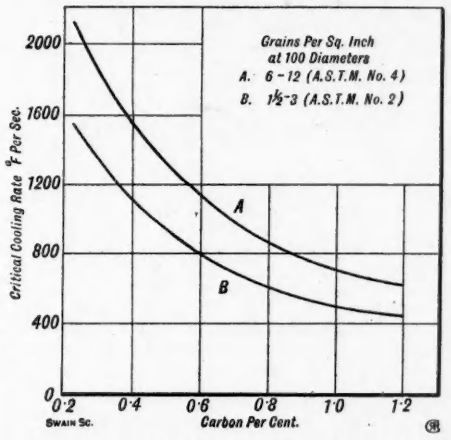

FIG. 2—*Relation of Critical Cooling Rate to Carbon Content of Iron-Carbon Alloys*

If R = critical cooling rate,
N = number of grains per square inch at 100 diameters,
C = carbon content,
it was found that for the range C = 0·23 to 1·21 per cent. and N between 20 and 1·5,

$$R = 410\ (N)^{0·4}/(C+0·2).$$

The independent influence of carbon content, chemical homogeneity, and grain size on the critical cooling rate, worked out in detail for these high-purity alloys is fundamental to the study of the corresponding effects in commercial steels. It may be expected that the same principles will hold, though the critical cooling rates are much slower and the austenitic grain size is influenced by various other factors which do not affect the high-purity alloys.

REFERENCES

[1] See THE METALLURGIST, August, 1938, 1937–38, 11, 145.
[2] See THE METALLURGIST, October, 1939, 1939–40, 12, 75.
[3] Bureau of Standards, Journal of Research, June, 1940, 1940, 24, 723.
[4] Trans. Amer. Soc. Steel Treating, 1924, 6, 251.
[5] Trans. Amer. Soc. for Metals, 1938, 26, 1.

Investigation of Carbides by the Methane Synthesis Method

A METHOD for the chemical investigation of the constitution of carbides was devised many years ago by Rudolf Schenck and called by him the "methane synthesis method." It is carried out by heating the finely divided metal at constant temperature for various times in contact with methane gas and finally determining the carbon content of the solid and the composition of the gas in equilibrium with it. Methane reacts with metals to form carbides in accordance with the following equation :

$$n\,M + CH_4 \rightleftarrows M_nC + 2H_2.$$

The gas in equilibrium with a definite carbide will therefore have a constant composition.

In an investigation by R. Schenck, F. Kurzer and H. Wesselkoch[1] chromium was heated in contact with methane at different temperatures and for various periods up to several weeks. Typical results indicating the composition of the gas in equilibrium with solids of different carbon content are given in Fig. 1. They provide evidence of changes in the constitution of the carbide at about 8·5 and 11·5 per cent.

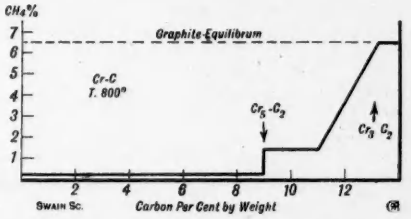

FIG. 1—*Carburising Isothermals for Chromium at 800 deg. Cent.*

of carbon. Below 8·5 per cent. of carbon, the solid consists of $Cr + Cr_5C_2$; between 8·5 and 11·5 of Cr_5C_2 and a solid solution, mainly Cr_3C_2. At 800 deg. Cent. the quantity of CH_4 in equilibrium with the chromium-carbon alloys containing more than 12·5 per cent. of carbon was the same as that in equilibrium with graphite, suggesting that Cr_3C_2 (carbon 13·3 per cent.) is dissociated at high temperatures with the liberation of carbon. The same authors found that the carburisation of tungsten by methane at 700 deg. Cent. gave rise to an unstable carbide corresponding to W_5C_2 (possibly $W_3C + W_2C$), with the probability of a transformation point between 700 deg. and 800 deg., since the indications were that at 800 deg. Cent. tungsten forms a stable carbide WC (see curve *h* in Fig. 3). Molybdenum at 800 deg. Cent. formed a single stable carbide Mo_2C. The carburisation of manganese was studied by R. Schenck, N. G. Schmahl and O. Ruetz.[2] Pure manganese carburised by methane formed

Mn_3C, dissolving about 0·5 per cent. of carbon at 800 deg. and at 900 deg. Cent. No other carbide was formed. A 50 : 50 alloy of manganese and iron gave rise to Mn_3C with an equivalent amount of Fe_3C. At 900 deg. Cent. this alloy exhibited a high solubility for carbon. In manganese-copper alloys carburisation was completely suppressed.

In their most recent work R. Schenck and K. Meyer[3] have applied the method of isothermal carburising by methane to the determination of the carbides formed by alloys of iron and tungsten. Isotherms for the following mixtures of the metallic components iron and tungsten were investigated :—

	Iron.	Tungsten.
a	20	1
b	10	1
c	2	1
d	1	1
e	1	2
f	1	10
g	1	25

The absorption was carried out as in previous work, but additional time was allowed in view of the unfavourable diffusion rates within the metallic

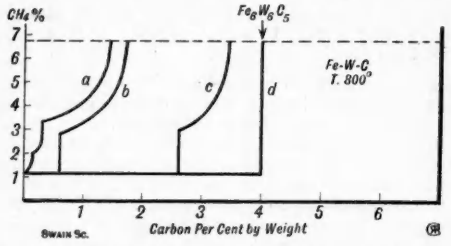

FIG. 2—*Carburising Isothermals for Mixtures of Iron and Tungsten at 800 deg. Cent.*
(*a*) 20 : 1. (*b*) 10 : 1. (*c*) 2 : 1. (*d*) 1 : 1.

particles. Slowness of attaining equilibrium is a characteristic of systems involving the metals having a very high melting point. The isotherms are shown in Figs. 2 and 3. In the latter appears also the isotherm (*h*) for pure tungsten, indicating a change in equilibrium at 6 per cent. of carbon (WC) ; below this the solid consists of W + WC and above 6 per cent. graphite is formed. In the equi-atomic mixture (*d*) graphite (equilibrium CH_4=6·5 per cent.) appears

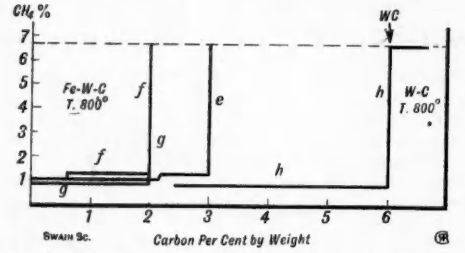

FIG. 3—*Carburising Isothermals for Mixtures of Iron and Tungsten and for Pure Tungsten at 800 deg. Cent.*
(*e*) 1 : 2. (*f*) 1 : 10. (*g*) 1 : 25. (*h*) Pure tungsten.

when the carbon exceeds 4 per cent. ($Fe_6W_6C_5$). When the Fe : W ratio is either greater or less than 1 graphite appears at a lower carbon content. The double carbide can be regarded as a compound of cementite and tungsten carbide, 2 Fe_3C, 3 W_2C.

From the carburising isothermals at 800 deg. Cent. a space model of the total isothermal could be constructed. Its projection in a plane, with limits of the phase fields, is shown in Fig. 4. The ordinates represent the number of carbon atoms for each 12 metal atoms and the abscissæ are atomic percentages of tungsten.

In field B the existing phases are α Fe, W and $Fe_6W_6C_5$. No division of this field appears to be caused by Fe_2W or Fe_3W in the iron-tungsten system. Possibly the heat of formation of such compounds is so small that they do not affect the $CH_4 : H_2$ equilibrium ratio, which is already very low (1·05 per cent. CH_4), to a measurable extent. In field A the phases are stated to be γ Fe + $Fe_6W_6C_5$; in D, W + $FeW_{23}C_7$; in C, W + $Fe_6W_6C_5$ + $FeW_{23}C_7$. In each case the metal phase contains carbon, and iron or tungsten, in solid solution. On the iron side (the region of the tungsten steels) there are three small fields E, F and G, probably characterised by α, α + γ and γ iron, but this portion of the diagram was not adequately worked out.

It is not clear why W_2C appears in the diagram reproduced in Fig. 4, as the indications of the isothermal *h* (Fig. 3) are in favour of WC. The carbide W_2C has never been detected in iron alloys, and for this reason S. Takeda used the pseudo-binary system $Fe_3C - W$ (not $Fe_3C - W_2C$) in the construction of his ternary diagram in which the compound Fe_3W_3C

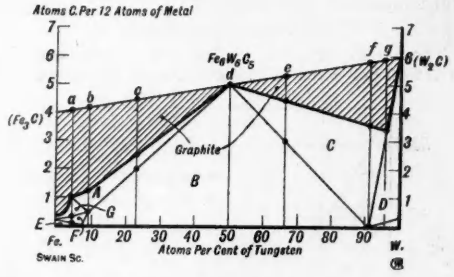

FIG. 4—*Projection of the Space Carburising Isothermal of Iron and Tungsten at 800 deg. Cent.*

found a place. This carbide was separated by electrolytic dissolution of an alloy with 1·2 per cent. of carbon and 30 per cent. of tungsten. A compound of the type $(Fe,W)_6C$ almost certainly exists in high-speed tool steel and, according to the X-ray analysis of Westgren, this is probably Fe_3W_3C with some of the tungsten replaced by iron. No trace of this compound is found by the methane synthesis method nor, on the other hand, is there any evidence of the existence of $Fe_6W_6C_5$ in steel, though its probable existence was recognised by Guillet and by Williams.

The methane synthesis method of investigation gives a view of the relation between metals and carbides which is not obtainable by other means. It applies only to equilibria at fairly high temperatures and does not provide direct evidence of the carbides present in steels or alloys at room temperature. It establishes the existence of certain carbides under the conditions of experiment. Some of these have a wide range of stability ; others are probably in the nature of solid solutions of carbon in carbides or in tungstides. The method can at the best be confirmatory in relation to the constitution of the alloy steels and cast irons.

REFERENCES

[1] *Zeit. anorg. allg. Chemie*, 1932, 203, 180.
[2] *Zeit. Electrochemie*, 1936, 42, 569.
[3] *Zeit. anorg. allg. Chemie*, 1940, 243, 259.